

Hydration in solution is critical for stable oxygen isotope fractionation between carbonate ion and water

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Abstract

Various isotope studies require accurate fractionation factors (α 's) between different chemical compounds in thermodynamic equilibrium. Although numerous isotope systems involve aqueous solutions, the conventional theory is formulated for the gas-phase and predicts incorrect α 's for many compounds dissolved in water. Here I show that quantum-chemistry calculations, which take into account solute–water interactions, accurately predict, for instance, oxygen isotope fractionation between dissolved CO_3^{2-} and H_2O (hereafter $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$). Simple force field and quantum-chemistry calculations for the ‘gas-phase’ ion CO_3^{2-} predict $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})} \simeq 1.015$ (15‰) at 25 °C. However, based on $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -clusters with up to 22 H_2O molecules, I calculate a value of 25‰, which agrees with the experimental value of $24.5 \pm 0.5\%$. Effects of geometry and anharmonicity on the calculated α were also examined. The calculations reveal the critical role of hydration in solution, which is ignored in the gas-phase theory. The approach presented provides an adequate framework for calculating fractionation factors involving dissolved compounds; it may also be used to predict α 's that cannot (or have not yet been) determined experimentally.

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1. INTRODUCTION

The chemistry of isotopes is of fundamental and practical significance to disciplines including physical chemistry, geo- and cosmochemistry, biochemistry, and many more (e.g. Driesner et al., 2000; Kubicki and Sykes, 2004; Boyet and Carlson, 2005; Hayes, 2006; Farquhar et al., 2007; Richter et al., 2007). The foundation of many isotope studies is an accurate knowledge of the isotope partitioning between different chemical compounds in thermodynamic equilibrium. The theoretical basis for calculating equilibrium constants of isotopic exchange reactions from first principles was formulated in the 1940s (Urey, 1947; Bigeleisen and Mayer, 1947) and has successfully been applied since then (for review, see e.g. Richet et al., 1977; Schauble, 2004). However, the conventional theory applies only to molecules in the gas-phase and fails to accurately

predict isotope fractionation factors (α 's) for many exchange reactions involving dissolved compounds in water.

For example, Urey (1947) predicted a value for the oxygen isotope fractionation between CO_3^{2-} and liquid water of $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})} \simeq 1.016$ at 25 °C. That is, CO_3^{2-} should be enriched in ^{18}O by about 16‰ relative to H_2O (see Section 2 for notation). However, the experimental value is $24.5 \pm 0.5\%$ (Beck et al., 2005). Thus, the conventional theory underestimates the observed value for the dissolved ion–water fractionation by more than 8‰. This is exceptionally large, given that calculations and measurements of true gas-phase equilibria often agree to within a few tenths of a per mil (Richet et al., 1977). Here I show that such large errors arise for dissolved compounds because the conventional gas-phase theory ignores effects of hydration, which is critical for the solute energy in aqueous solution. I employ a theoretical framework using quantum-chemistry calculations of solute–water clusters that accurately predict isotopic fractionation factors involving dissolved compounds in water. The cluster calculations

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include a significant number of H₂O molecules in the first few hydration shells of the solute. This has only recently become possible due to progress in computational performance (see e.g. Yamahira and Oi, 2004; Liu and Tossell, 2005; Rustad et al., 2008).

The paper is organized as follows. Three fundamentally different theoretical methods to determine the oxygen isotope fractionation between carbonate ion and water are introduced in Section 2. They are: (A) simple force field calculations of the isolated ('gas-phase') CO₃²⁻-ion, (B) quantum-chemistry computations of the isolated CO₃²⁻-ion, and (C) quantum-chemistry computations of the hydrated CO₃²⁻ · (H₂O)_n-ion. Definitions, notation, and an approach to assess anharmonicity effects on $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$ are also described in Section 2. The results of the calculations and the predicted temperature dependence of $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$ are presented in Section 3. The sensitivity of the calculations to basis set, cluster geometry, and anharmonicity are discussed in Section 4. Finally, I conclude that the theoretical approach described here (C: quantum-chemistry computations of the hydrated solute) provides a means of calculating reliable fractionation factors of dissolved compounds based on first principles (Section 5). Mathematical formulae for the simple force fields are given in Appendices A and B. Appendix C provides a general discussion of the relationship between fractionation factor and temperature.

2. METHODS

2.1. Notation and fractionation factor

The stable isotope fractionation factor between two compounds A and B is given by $\alpha_{(A-B)} = R_A/R_B$, where R 's are isotope ratios of the element of interest in the respective compounds (e.g. in case of oxygen in water $R_{\text{H}_2\text{O}} = [\text{H}_2^{18}\text{O}]/[\text{H}_2^{16}\text{O}]$). The fractionation is expressed in per mil using $\epsilon_{(A-B)} = (\alpha_{(A-B)} - 1) \times 10^3$ or $10^3 \times \ln \alpha_{(A-B)}$. The δ -value of a sample A is $\delta_A = (R_A/R_{\text{std}} - 1) \times 1000$, where R_{std} is the isotope ratio of the standard.

Isotopic fractionation factors are calculated from first principles based on differences in the vibrational energy of molecules. Fundamental frequencies and molecular forces are usually determined based on spectroscopic data and mechanical molecular models, or – more recently – using computational methods such as *ab initio* molecular orbital theory (AIMOT) (e.g. Jensen, 2004). Fractionation factors were calculated from reduced partition function ratios (Urey, 1947):

$$\left(\frac{Q'}{Q}\right)_r = \frac{s}{s'} \prod_i \frac{u_i' \exp(-u_i'/2)}{u_i \exp(-u_i/2)} \frac{1 - \exp(-u_i)}{1 - \exp(-u_i')}, \quad (1)$$

with s and s' being symmetry numbers, $u_i = hc\omega_i/kT$ and $u_i' = hc\omega_i'/kT$ where h is Planck's constant, c is the speed of light, k is Boltzmann's constant, T is temperature in Kelvin, and ω_i and ω_i' are the frequencies of the isotopic molecules or the solute–water clusters.

The theoretical calculations yield β -factors of the solute and H₂O(g) and thus the fractionation relative to water vapor. In the present case, the β -factor of a compound A is given by:

$$\beta_A = \left(\frac{Q'_A}{Q_A}\right)_r^{\frac{1}{k}}, \quad (2)$$

where k is the number of atoms being exchanged. The fractionation relative to liquid water was obtained using the observed water vapor–liquid water ¹⁸O fractionation at a given temperature (Majoube, 1971). For example, at the HF/6-31G(d) level of theory (see below), the fractionation factor between CO₃²⁻ · (H₂O)₂₂ and H₂O(l) at 25 °C was calculated as:

$$\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O}(l))} = \frac{\beta_{(\text{CO}_3^{2-}-\text{H}_2\text{O}(l))}}{\beta_{(\text{H}_2\text{O}(g))}} \frac{1}{\alpha_{(\text{H}_2\text{O}(l)-\text{H}_2\text{O}(g))}}, \quad (3)$$

$$= \frac{1.1035}{1.0665} \frac{1}{1.0094} = 1.025 \quad (25\text{‰}). \quad (4)$$

2.2. Theoretical methods to determine α

As mentioned above, three different methods were used to determine $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$. (A) Simple force field calculations of the isolated ('gas-phase') CO₃²⁻-ion, (B) quantum-chemistry computations of the isolated CO₃²⁻-ion, and (C) quantum-chemistry computations of the hydrated CO₃²⁻ · (H₂O)_n-ion. The α value based on method (A) has been widely cited since the original work by Urey (1947). However, the method significantly underestimates α . I will examine whether different force field assumptions and/or different sets of frequencies yield results closer to the experimental value. This turned out not to be the case. Method (B) predicts similar values and shows that the incorrect theoretical α 's are unlikely due differences between the traditional and quantum-chemical treatment of the isolated ion. Finally, method (C) shows that the problem can be solved by including effects on α due to hydration of the dissolved CO₃²⁻-ion in solution.

The hypothetical gas-phase CO₃²⁻-ion is a planar molecule of type XY₃ with 6 normal modes (Table 1) and D_{3h} symmetry (see central molecule in Fig. 2). For this type of molecule, simple force field calculations can be performed

Table 1
Frequencies (in cm⁻¹) of H₂¹⁶O(g) given by Richet et al. (1977) and of the C¹⁶O₃²⁻-ion^a given by different authors.

	ω_1	ω_2	ω_3	ω_4
Assignment ^b	sstr	sb	asstr	
H ₂ ¹⁶ O(g)	3835.37	1647.59	3938.74	
Assignment	sstr	opb	asstr	ipb
C ¹⁶ O ₃ ^{2-c}	1087	878	1437(2)	714 (2)
C ¹⁶ O ₃ ^{2-d}	1070	881	1460(2)	712 (2)
C ¹⁶ O ₃ ^{2-e}	1064	880	1380/1436	684 (2)

^a Twofold degeneracy indicated by '(2)'.
^b Assignment: sstr = symmetric stretch, sb = symmetric bend, asstr = asymmetric stretch, opb = out-of-plane bend, ipb = in-plane bend.
^c Urey and Greiff (1935) and Urey (1947): "Estimated by Dr. Jennie Rosenthal".
^d C¹⁶O₃²⁻ in the calcite lattice (Bottinga, 1968).
^e C¹⁶O₃²⁻ in water (Davis and Oliver, 1972). Values are nearly identical to more recent results (Rudolph et al., 2006).

to determine α (Section 2.2.1, Appendices A and B). Note that quantum-chemistry computations predict spontaneous ionization of the isolated CO_3^{2-} -ion (electronically unstable); the carbonate ion should therefore not exist in the gas phase (Janoschek, 1992; Boldyrev et al., 1996). This suggests that for this molecule, gas-phase calculations to determine α may be inappropriate. Nevertheless, the force field calculations for the gas-phase ion below will allow comparison to previous force field calculations (Urey, 1947; Janz and Mikawa, 1960), as well as comparison to the quantum-chemistry approach used here.

The carbonate ion is known to exist as a dissolved ion in aqueous solution, representing an important component of the CO_2 system in natural waters (Davis and Oliver, 1972; Zeebe and Wolf-Gladrow, 2001). When dissolved in water, the interaction between solute and solvent leads to association of a significant number of water molecules with the ion, forming the hydration shell (e.g. Leung et al., 2007; Kumar et al., 2009). This affects physico-chemical properties of the ion, including its fundamental vibrational modes. For example, the highest CO_3 -frequency (asymmetric stretch, single peak in D_{3h} symmetry) splits into two bands in the solution (Davis and Oliver, 1972; Rudolph et al., 2006). Furthermore, hydration adds a number of cluster-modes of the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ entity to the spectrum, which do not exist in D_{3h} symmetry. This in turn affects the reduced partition function ratio and thus the isotope partitioning between carbonate ion and water, as shown below.

2.2.1. Simple force fields

The most important quantities that enter Eq. (1) are the fundamental vibrational frequencies, ω , of a molecule of a given chemical formula and those of the isotopically substituted molecule, ω' . One way to determine ω and ω' is to experimentally measure either one of the two frequencies by infrared and/or Raman spectroscopy from which the force constants in the molecule are determined, which is then used to calculate the other frequency. For the $\text{C}^{16}\text{O}_3^{2-}$ -ion, I have used frequencies based on observed ω 's in the calcite lattice and in solution, and ω' 's based on theoretical estimates (Table 1). It turned out that the choice of the $\text{C}^{16}\text{O}_3^{2-}$ -frequencies does not have a dominant effect on the calculated α .

For polyatomic molecules, force field methods such as simple central forces, simple valence forces, generalized valence force fields (GVFF) and Urey–Bradley force fields (UBFF) are often employed. I have calculated frequencies of the isotopically substituted CO_3^{2-} -molecule based on GVFF and UBFF (cf. Herzberg, 1966; Ross, 1972; Nakamoto, 1997). The details of the calculations are given in Appendices A and B. In summary, given experimental frequencies (Table 1), the molecular force constants and thus the frequencies of the isotopically substituted molecule can be determined. The fractionation factor α is then calculated using Eq. (1).

2.2.2. Quantum-chemistry calculations

Numerical frequencies were calculated using the quantum-chemistry package GAMESS (Gordon and Schmidt, 2005) in parallel execution on a 12-CPU Linux cluster after geometry optimization. Geometric stability was inferred

from the absence of imaginary eigenvalues in the Hessian matrix. Numerical frequencies were scaled by a scaling factor based on least-squares fits between observed frequencies of water vapor and solute (Table 1) and those calculated for water vapor and the largest solute–water cluster for a given basis set and level of theory (Fig. 1). It is well known that the different quantum-chemistry methods systematically over- or underestimate molecular frequencies (Scott and Radom, 1996), which can lead to errors in the calculated α . For example, at the HF/6-31G(d) level of theory, bond lengths are usually too short and corresponding frequencies systematically too high (Jensen, 2004). The calculated frequencies were therefore scaled by the scaling factor obtained for the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -water system studied here. At the HF/6-31G(d) level of theory (see Gordon and Schmidt, 2005; Jensen, 2004), the root-mean-square (rms) error of individual fits for the CO_3^{2-} -cluster and H_2O at HF/6-31G(d) were 30 and 40 cm^{-1} . The scaling procedure yielded a scaling factor of 0.925 for the combined carbonate ion and water frequencies. Note that this value was used here rather than the average value given by Scott and Radom (1996) for HF/6-31G(d). The former was obtained here specifically for the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -water frequencies and should be more accurate for the current purpose. The scaling factor for a given basis set and level of theory was used to scale ω 's and calculate α 's for all solute–water clusters.

Density functional theory methods were also tested including diffuse functions [for instance, B3-LYP/6-31+G(d) (see Gordon and Schmidt, 2005; Jensen, 2004)]. This had a minor effect on calculated α 's, provided that appropriate scaling factors were used (see above). At B3-LYP/6-31+G(d), the scaling procedure for the frequencies of the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{22}$ -cluster and water yielded a scaling factor of 1.021 and individual rms errors of 23 and 35 cm^{-1} .

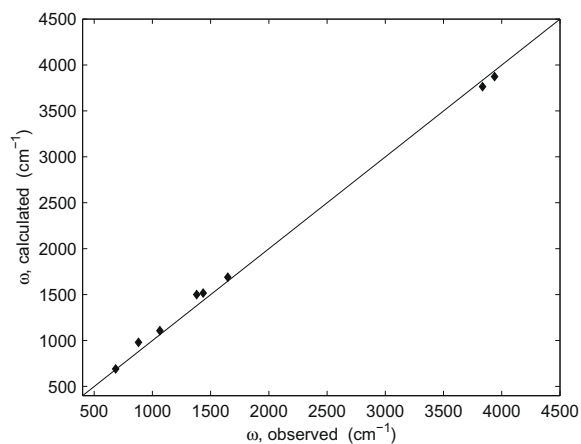


Fig. 1. Comparison between observed frequencies of dissolved CO_3^{2-} and water vapor (Davis and Oliver, 1972; Richet et al., 1977; Rudolph et al., 2006) and those calculated and scaled for $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{22}$ and water vapor at the HF/6-31G(d) level of theory. For the calculation of $\alpha_{(\text{CO}_3^{2-} \cdot \text{H}_2\text{O})}$, scaled numerical frequencies were used based on the scaling factor obtained from the least-squares fit between observed and calculated ω 's (Scott and Radom, 1996).

2.3. Anharmonicity

Anharmonicity effects on the calculated α were also examined. It is noted that simply inserting anharmonic frequencies into Eq. (1) to calculate α is incorrect because the formula is based on the harmonic approximation by definition. Instead, anharmonicity effects were treated as follows. Including quartic terms in the potential energy, the anharmonic zero-point energy contribution to the partition function ratio for polyatomic molecules may be written as (Richet et al., 1977):

$$\left(\frac{Q'}{Q}\right)_{\text{anh}}^0 = \exp\left[-\frac{hc}{kT} \sum_{i \leq j} (x'_{ij} - x_{ij}) / 4\right], \quad (5)$$

where x_{ij} are anharmonic constants (in cm^{-1}), which are often negative for higher fundamentals. Note that the contribution due to anharmonicity of excited vibrational states is usually small at room temperature and will be neglected. Unfortunately, the x_{ij} are generally unknown for large molecules. However, if harmonic and anharmonic ω 's have been calculated numerically, Eq. (5) can be evaluated without knowing the individual x_{ij} . The relationship between harmonic (ω_i) and anharmonic frequencies (superscript a) may be approximated by (Herzberg, 1966):

$$\omega_i^a = \omega_i + x_{ii} + \frac{1}{2} \sum_{j \neq i} x_{ij} = \omega_i + \Delta x_i, \quad (6)$$

where $x_{ij} = x_{ji}$. The sum over all differences between ω_i^a and ω_i is:

$$\sum (\omega_i^a - \omega_i) = \sum \Delta x_i = \sum_{i \leq j} x_{ij}, \quad (7)$$

which is just the sum required to evaluate Eq. (5). Thus given harmonic and anharmonic frequencies of a molecule and its isotopologue (e.g. obtained using quantum-chemistry packages), the anharmonic contribution to the partition function ratio and thus to α may be calculated.

Anharmonic frequencies for $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ were obtained using the quartic force field approximation (Gordon and Schmidt, 2005) with and without 2-mode coupling for up to $n = 3$ and $n = 10$, respectively. Note that the calculations are computationally very expensive, particularly when mode coupling is included. Anharmonic corrections to α computed for $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$, $n \leq 10$ using GAMESS without mode coupling were consistently smaller than 0.9‰ (see Section 3). Additional corrections due to 2-mode coupling ($n \leq 3$) were larger (up to 2‰) and more variable, depending on n , the method (e.g. HF/6-31G(d) vs. MP2/6-31G(d)), and coordinate choice [e.g. Cartesian vs. internal (Z-matrix)].

3. RESULTS

I have determined stable geometries of $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -clusters with up to 22 H_2O molecules based on quantum-chemistry calculations (Fig. 2). In contrast to the hypothetical gas-phase CO_3^{2-} -ion with 6 normal modes (D_{3h} symmetry), the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{22}$ -cluster has 204 normal modes (C_1 symmetry). None of the calculated frequencies is imaginary, indicating a minimum on the potential energy surface, i.e.

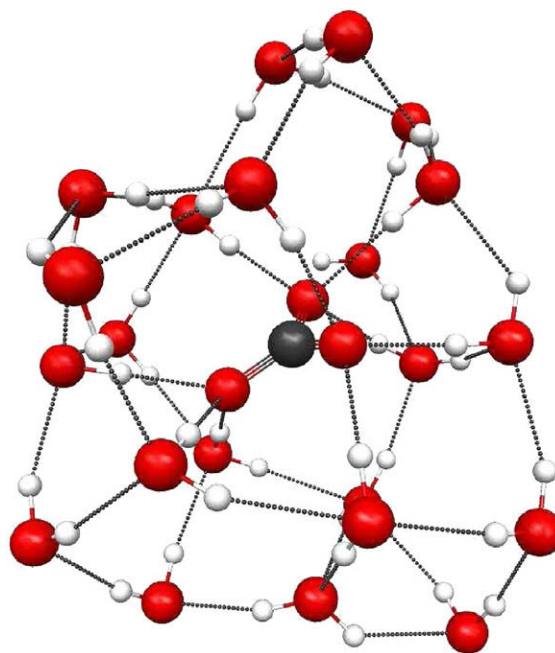


Fig. 2. Optimized geometry of a hydrated carbonate ion (center) including 22 water molecules (C_1 symmetry) based on Hartree–Fock theory (see Section 2) calculated with the quantum-chemistry package GAMESS (Gordon and Schmidt, 2005). Black: carbon, red: oxygen, white: hydrogen. Dotted lines indicate hydrogen bonds.

geometric stability. The highest CO_3 -frequency (asymmetric stretch, single peak in D_{3h} symmetry) splits into two bands in the cluster, in agreement with observations (Davis and Oliver, 1972; Rudolph et al., 2006). The predicted oxygen isotope enrichment for the ‘gas-phase’ CO_3^{2-} -ion and the dissolved $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{22}$ -ion relative to H_2O at 25 °C are 13‰ and 25‰, respectively (Fig. 3).

The simple force field calculations (Fig. 3, lower gray area) are based on general valence forces (GVFF) and Urey–Bradley force fields (UBFF) (Urey, 1947; Zeebe, 2005). They yield ε -values between 13‰ and 17‰ for the isolated CO_3^{2-} -ion at 25 °C. Note that for water, the β -factor of the HF/6-31G(d) calculation was used here to allow comparison with the quantum-chemistry results. The force field results include GVFF and frequencies (ω 's) from Urey (1947): 16.6‰ (see Table 1 for ω 's), GVFF and ω 's from Bottinga (1968) and Chacko et al. (1991) for CO_3^{2-} in the calcite lattice: 16.4‰, GVFF and ω 's from Davis and Oliver (1972) for dissolved CO_3^{2-} : 16.8‰, UBFF and ω 's from Bottinga (1968) for CO_3^{2-} in the calcite lattice: 15.5‰, and UBFF and ω 's from Davis and Oliver (1972) for dissolved CO_3^{2-} : 13.2‰.

Thus the force field values are close to the corresponding results of the quantum-chemistry calculations for the isolated ion. Note that the latter approach predicts spontaneous ionization of the isolated CO_3^{2-} -ion (electronically unstable); the carbonate ion should therefore not exist in the gas phase (Janoschek, 1992; Boldyrev et al., 1996). The computed fractionation factor increases with the number of water molecules in the cluster (n) but reaches a limit above a certain cluster size (Fig. 3). Adding more H_2O mol-

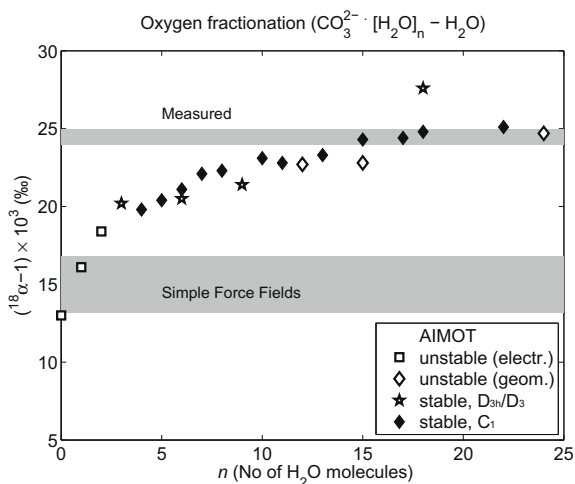


Fig. 3. Oxygen isotope fractionation between carbonate ion and water at 25 °C. The experimental value of $24.5 \pm 0.5\text{‰}$ is indicated by the upper gray bar (Beck et al., 2005). The lower gray bar shows values calculated based on general valence forces and Urey–Bradley force fields (Urey, 1947; Zeebe, 2005). Values based on quantum-chemistry calculations (*ab initio* molecular orbital theory, AIMOT) are shown as a function of the number of H_2O molecules in the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -cluster. The final theoretical α as calculated here is the limiting value for large n of the lowest energy conformer that is electronically and geometrically stable (see arrow).

ecules beyond a certain n has little effect on α because the influence of a water molecule in the outer hydration shell on the oxygen bonds of the central CO_3 -group decreases with increasing distance between them. Note that the calculated α for the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{18}$ -cluster is larger for the D_{3h} -symmetry conformer than for the C_1 conformer (Fig. 3). However, the C_1 conformer has a lower energy, which is a more favorable geometry in thermodynamic equilibrium. The final theoretical α is given by the limiting value at large n of the lowest energy conformer that is electronically and geometrically stable (here 25‰ at C_1 symmetry and 25 °C). This value agrees with the experimental value of $24.5 \pm 0.5\text{‰}$ within errors (Beck et al., 2005).

3.1. Temperature dependence

As described above, the calculated fractionation factor at a given temperature is much larger for the dissolved ion than for the hypothetical ‘gas-phase’ ion. In addition, the calculated temperature dependence of $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$ for the carbonate ion–water cluster is significantly steeper than for the ‘gas-phase’ ion (Fig. 4). Over the temperature range 0–300 °C, α drops by $\sim 27\text{‰}$ and $\sim 16\text{‰}$ for the dissolved and isolated ion, respectively. Note also that the theoretical relationship between $10^3 \times \ln [\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}]$ and temperature is non-linear when plotted vs. $1/T^2$. The $1/T^2$ relationship used to fit experimental data in the range 15–40 °C should therefore not be extrapolated to other temperatures. The fractionation factor is approximately linear in $1/T$ and $1/T^2$ only within certain temperature ranges. However, over the entire temperature range this is generally not the case (see Appendix C).

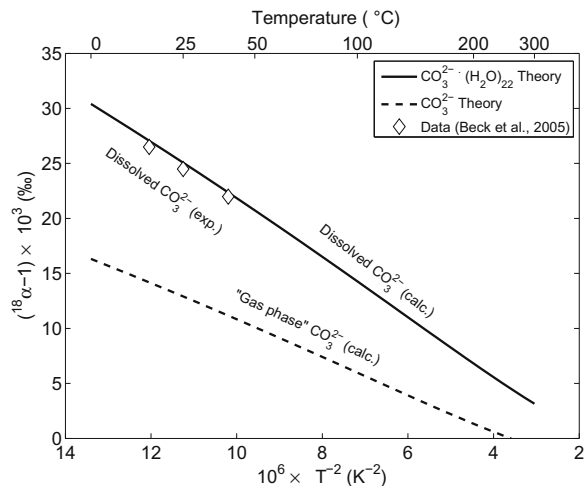


Fig. 4. Oxygen isotope fractionation between carbonate ion and water as a function of temperature. The dashed and solid line show the values for $\alpha_{(\text{CO}_3^{2-}-\text{H}_2\text{O})}$ calculated here for the isolated ion (“gas-phase”) and carbonate ion–water clusters ($n=22$), respectively, based on *ab initio* molecular orbital theory. Diamonds show experimental values at 15, 25, and 40 °C (Beck et al., 2005).

4. DISCUSSION

As shown above, the calculated oxygen isotope fractionation for the ‘gas-phase’ CO_3^{2-} -ion and the dissolved $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{22}$ -ion relative to H_2O are 13‰ and 25‰, respectively (Fig. 3). In other words, the calculated α nearly doubles due to hydration (Fig. 2). This difference in α could be due to (a) stronger overall fractionation between the hydrated $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -ion and bulk water and/or (b) stronger fractionation between the CO_3 -skeleton and bulk water. Case (b) may be examined by recalculating the fractionation factor using only the frequencies of the hydrated ion that fall within the range of the skeletal CO_3 modes (corresponding to the fundamental XY_3 modes, see Table 1). This yields an α of $\sim 16.5\text{‰}$, i.e. 3.5‰ heavier than the gas-phase calculation. The remaining 8.5‰ are due to other $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{22}$ -cluster modes that involve the oxygen of the CO_3 group. These frequencies fall mostly below the lowest CO_3 skeletal mode (in-plane-bend at $\sim 680 \text{ cm}^{-1}$). As a result, for the calculated α in solution, the overall fractionation between the hydrated $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -ion and bulk water is more important than changes in the fractionation between the CO_3 -skeleton and bulk water.

I have also tested whether the calculations indicate ^{18}O -enrichment of the water within the hydration shell of the ion. The reduced partition function ratios showed little difference for water molecules within the first or second hydration shell and were similar to those obtained for pure water clusters with up to eight water molecules. In general, when compared to calculated reduced partition function ratios for water vapor, the ratios obtained for water in the hydration shell of the ion and for the pure water clusters were consistent with those expected from the observed water vapor–liquid water ^{18}O fractionation (Majoube, 1971). Thus, the quantum-chemical calculations presented here do not

indicate significant differences between the $^{18}\text{O}/^{16}\text{O}$ ratios of the hydrated water in the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -cluster and the bulk water. This result appears to be consistent with observations that oxygen isotope effects in H_2O in the hydration shells of cations are much larger than in anions (e.g. Taube, 1954).

4.1. Basis set and level of theory

The quantum-chemistry calculations used here to determine fractionation factors (see Section 2) are based on Hartree–Fock theory [see Jensen (2004) and Gordon and Schmidt (2005) and reference cited therein]. Other methods are available, which mostly differ in the size of the set of mathematical functions used to describe the molecular orbitals (basis set) and the treatment of electron correlation (level of theory). The question arises whether or not the results presented here are method-specific. It is well known that the different quantum-chemistry methods systematically over- or underestimate molecular frequencies (Scott and Radom, 1996). The calculated frequencies are therefore scaled by a specific scaling factor obtained from least-squares fits of calculated vs. observed frequencies (for values and root-mean-square errors obtained in this study, see Section 2). I have tested the most successful methods for predicting molecular frequencies including Hartree–Fock theory and density functional theory (Scott and Radom, 1996), with and without diffuse functions. Diffuse functions account for the long-range behavior of molecular orbitals and are potentially important when anions are involved (Jensen, 2004). However, it appears that for the current system, the quantum-chemistry method used is of minor importance, provided that appropriate scaling factors are used. For example, for the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ -cluster at $n = 10$ and $n = 22$, the calculated α differs by 0.3‰ and 0.5‰, respectively, between a Hartree–Fock method with a standard basis set and a density functional theory method including diffuse functions (see Section 2).

4.2. Cluster geometry and anharmonicity

I have also tested the sensitivity of the calculated fractionation factor to the cluster geometry. Several configurations of the $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_{22}$ -cluster with different energies were optimized at C_1 symmetry. The difference in α between the two lowest energy conformer was ~ 1 ‰. The total range between all clusters was ~ 2 ‰. However, this included conformer with substantially higher energy. Thus, the sensitivity to cluster symmetry appears to be small, provided that similar (low) energy conformer are used in the calculation.

Another potential source of uncertainty in the calculations is the use of quadratic terms only in the potential energy (harmonic approximation), which neglects higher order terms (anharmonicity). First, it is important to note that simply using Eq. (1) with anharmonic frequencies is incorrect because the formula is based on the harmonic approximation by definition. However, if harmonic and anharmonic frequencies can be obtained (e.g. from quantum-chemistry packages), a revised expression may be used to correct for anharmonicity effects on the calculated α (see

Section 2). Anharmonic frequencies for $\text{CO}_3^{2-} \cdot (\text{H}_2\text{O})_n$ were calculated using the quartic force field approximation (Gordon and Schmidt, 2005) with and without 2-mode coupling for up to $n = 3$ and $n = 10$, respectively. Note that the calculations are computationally very expensive. Note also that the method implemented in the quantum-chemistry package GAMESS (Gordon and Schmidt, 2005), for instance, is limited to molecular systems of up to 12–15 atoms and is less accurate for weak intermolecular vibrations of hydrogen-bonded clusters (Chaban et al., 2000). The calculated effect on α was 0.7‰ at $n = 10$ without mode coupling and less than 0.9‰ for all n tested. For $n \leq 3$, mode coupling was included, which added corrections of up to ~ 2 ‰ to these values (see Section 2). Thus within the methodological limits mentioned above, anharmonicity does not appear to have a dominant effect on the calculated α -values for the system tested.

5. CONCLUSIONS

A theoretical framework for accurate predictions of fractionation factors involving dissolved compounds is both of fundamental and practical significance. For instance, understanding isotope fractionation in the dissolved carbonate system is critical for areas including ocean uptake of anthropogenic CO_2 , biomineralization, and climate reconstructions (Zeebe and Wolf-Gladrow, 2001; Beck et al., 2005). The stable oxygen isotope fractionation between $\text{HCO}_3^-/\text{CO}_3^{2-}$ and water, for example, plays a critical role in a recent debate about the primary driver of Phanerozoic climate change (Spero et al., 1997; Zeebe, 1999; Shaviv and Veizer, 2003; Rahmstorf et al., 2004).

In general, the theoretical approach used here should be applicable to any isotope system involving dissolved compounds. It provides a means of calculating thermodynamic properties of dissolved compounds (including dissolved gases, ions, metal complexes, etc.) based on which reliable fractionation factors can be derived from first principles. The theory may therefore be used to predict α -values of exchange reactions that cannot (or have not yet been) determined experimentally. The expected advances in computational performance in the future will enable application of the current approach to significantly larger and more complex systems.

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APPENDIX A. GENERALIZED VALENCE FORCE FIELDS (GVFF)

In the framework of GVFF, the GF matrix method is used (Wilson, 1939, 1941). The frequencies of molecular vibration are related to the forces in the molecule by the matrix secular equation:

$$|\mathbf{GF} - E\lambda| = 0, \quad (\text{A.1})$$

where the \mathbf{G} matrix depends on the atomic masses and molecular geometry (see below), \mathbf{F} contains the force constants, \mathbf{E} is the identity matrix, and $\lambda_i = 4\pi^2 c^2 \omega_i^2$ are the eigenvalues of \mathbf{GF} . The \mathbf{G} and \mathbf{F} matrices for a XY_3 molecule of D_{3h} symmetry can be written as:

$$\mathbf{G} = \begin{pmatrix} G_{11} & 0 & 0 & 0 \\ 0 & G_{22} & 0 & 0 \\ 0 & 0 & G_{33} & G_{34} \\ 0 & 0 & G_{34} & G_{44} \end{pmatrix};$$

$$\mathbf{F} = \begin{pmatrix} F_{11} & 0 & 0 & 0 \\ 0 & F_{22} & 0 & 0 \\ 0 & 0 & F_{33} & F_{34} \\ 0 & 0 & F_{34} & F_{44} \end{pmatrix}, \quad (\text{A.2})$$

with $G_{11} = \mu_y$, $G_{22} = (3/d^2)(\mu_y + 3\mu_x)$, $G_{33} = \mu_y + 3\mu_x/2$, $G_{34} = (3\sqrt{3}/2d)\mu_x$, $G_{44} = (3/d^2)(\mu_y + 3\mu_x/2)$, where μ_i 's are the reciprocal masses of X and Y and d is the bond distance. From the secular equation (Eq. (A.1)), F_{11} and F_{22} can be calculated as $F_{11} = \lambda_1/G_{11}$ and $F_{22} = \lambda_2/G_{22}$ using $\lambda_i = 4\pi^2 c^2 \omega_i^2$, where the ω_i 's are taken from the literature, including experimental results (Table 1). The force constants F_{33} , F_{34} and F_{44} are determined from:

$$F_{33}G_{33} + F_{44}G_{44} + 2F_{34}G_{34} = \lambda_3 + \lambda_4, \quad (\text{A.3})$$

$$\begin{vmatrix} G_{33} & G_{34} & F_{33} & F_{34} \\ G_{34} & G_{44} & F_{34} & F_{44} \end{vmatrix} = \lambda_3 \lambda_4, \quad (\text{A.4})$$

using the assumption that the ratio of force constants and kinetic constants is the same (Thirugnanasambandam and Srinivasan, 1969; Zeebe, 2005). From the molecular force constants, the frequencies of isotopically substituted molecules are determined; the fractionation factor α is then calculated using Eq. (1).

APPENDIX B. UREY-BRADLEY FORCE FIELDS (UBFF)

In the framework of UBFF, the four force constants K , H , F , and F' for the in-plane vibrations of planar XY_3 molecules (see Janz and Mikawa, 1960) have to be determined from three frequencies using

$$F' = \gamma F. \quad (\text{B.1})$$

Janz and Mikawa (1960) showed that $\gamma = -1/10$ or $-1/13$ works well for various types of XY_3 molecules. The equations for the normal frequencies are (note that the Φ_{ii} used below are different from the F_{ii} used in GVFF):

$$\lambda_1 = G_{11}\Phi_{11}, \quad (\text{B.2})$$

$$\lambda_3 + \lambda_4 = G_{33}\Phi_{33} - (9/4)G_{34}\Phi_{34} + G_{44}\Phi_{44} =: s, \quad (\text{B.3})$$

$$\lambda_3\lambda_4 = (\Phi_{33}\Phi_{44} - (3/16)\Phi_{34}^2)GG =: p, \quad (\text{B.4})$$

where $G_{11} = \mu_y$, $G_{33} = (3/2)\mu_x + \mu_y$, $G_{34} = \mu_x$, $G_{44} = (9/2)\mu_x + 3\mu_y$, $GG = 3\mu_y^2 + 9\mu_x\mu_y$, and $\Phi_{11} = K + 3F$, $\Phi_{33} = K + (3/4)F' + (3/4)F$, $\Phi_{34} = F' + F$, $\Phi_{44} = H - (3/4)F' + (1/4)F$.

Using Eq. (B.1) and eliminating Φ_{44} (essentially H), yields a quadratic equation for F :

$$a_2 F^2 + a_1 F + a_0 = 0, \quad (\text{B.5})$$

with

$$a_2 = -\frac{1}{16} \left[9(\gamma - 3)^2 G_{33} + 27(\gamma - 3)(\gamma + 1)G_{34} - 3(\gamma + 1)^2 G_{44} \right], \quad (\text{B.6})$$

$$a_1 = \frac{1}{4} \left[3(\gamma - 3)s - 6(\gamma - 3)\lambda_1 G_{33}/\mu_y + 9(\gamma + 1)\lambda_1 G_{34}/\mu_y \right], \quad (\text{B.7})$$

$$a_0 = s\lambda_1/\mu_y - (\lambda_1/\mu_y)^2 G_{33} - p G_{44}/GG. \quad (\text{B.8})$$

Once this equation is solved, F' is determined from Eq. (B.1). Furthermore,

$$\Phi_{33} = (\lambda_1/\mu_y) + 3F(\gamma - 3)/4, \quad (\text{B.10})$$

$$\Phi_{34} = F(\gamma + 1), \quad (\text{B.11})$$

$$\Phi_{44} = (p/GG + 3\Phi_{34}^2/16)/\Phi_{33}, \quad (\text{B.12})$$

and finally:

$$K = (\lambda_1/\mu_y) - 3F, \quad (\text{B.13})$$

$$H = \Phi_{44} + F(3\gamma - 1)/4, \quad (\text{B.14})$$

from which all force constants K , H , F , and F' were calculated. From the molecular force constants, the frequencies of isotopically substituted molecules are determined; the fractionation factor α is then calculated using Eq. (1).

APPENDIX C. TEMPERATURE DEPENDENCE OF FRACTIONATION FACTOR

It can be shown that the fractionation factor (more precisely $10^3 \times \ln \alpha$) is approximately linear in $1/T$ and $1/T^2$ within certain temperature ranges. However, over the entire temperature range this is generally not the case, as illustrated in the following for an isotopic exchange reaction between diatomic molecules. Diatomics were chosen in this example (rather than carbonate ion and water) because the formulas are less complicated and the $1/T$ and $1/T^2$ dependence of $10^3 \times \ln \alpha$ is more obvious.

The reduced partition function ratio for diatomics reads (subscript r will be omitted):

$$\left(\frac{Q'}{Q}\right) = \frac{s}{s'} \frac{u'}{u} \frac{\exp(-u'/2)}{\exp(-u/2)} \frac{1 - \exp(-u)}{1 - \exp(-u')}, \quad (\text{C.1})$$

where $u = hc\omega/kT$, and ω and ω' are the frequencies of the isotopic molecules (for other symbols, see Eq. (1)). Thus (Q'/Q) and α are in general non-linear functions of u or $1/T$. However, at low temperatures or high frequencies, Eq. (C.1) may be approximated by (Bigeleisen and Mayer, 1947; Urey, 1947; Criss, 1999):

$$\ln \left(\frac{Q'}{Q}\right) = \ln \left(\frac{s}{s'} \frac{\omega'}{\omega}\right) + \frac{u - u'}{2}. \quad (\text{C.2})$$

At high temperatures, Eq. (C.1) may be approximated by:

$$\ln \left(\frac{s'}{s} \frac{Q'}{Q}\right) = \frac{u^2 - u'^2}{24}. \quad (\text{C.3})$$

Because u is proportional to $1/T$, the natural logarithm of the partition function ratio and $10^3 \times \ln \alpha$ is linear in $1/T$ and $1/T^2$ at low and high temperatures, respectively. This behavior is illustrated in Fig. C.1, in which $10^3 \times \ln \alpha$ is

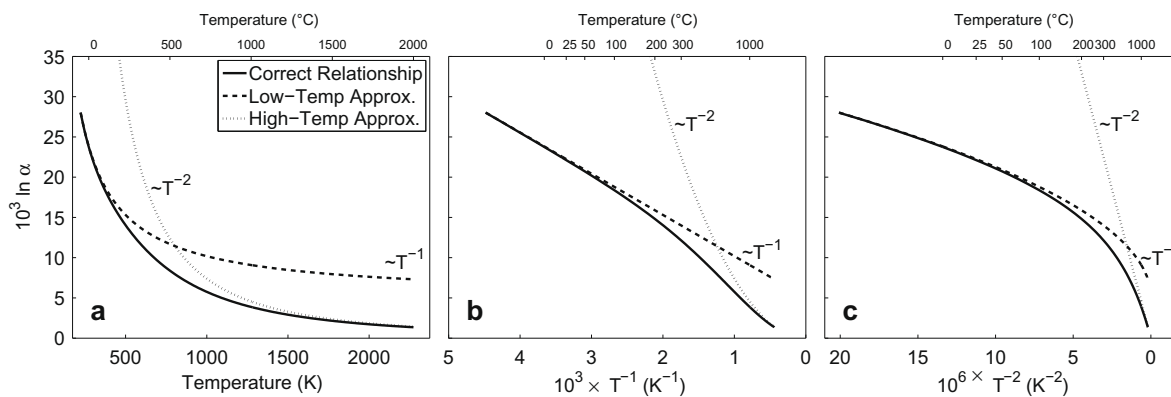


Fig. C.1. Illustration of the temperature dependence of $10^3 \times \ln \alpha$ for an isotopic exchange reaction between diatomic molecules. (a) Correct relationship (solid line, Eq. (C.1)), low temperature approximation ($\propto 1/T$, dashed line, Eq. (C.2)), and high temperature approximation ($\propto 1/T^2$, dotted line, Eq. (C.3)), as a function of temperature in $^{\circ}\text{C}$ and in Kelvin. (b) As a function of $1/T$. (c) As a function of $1/T^2$. The fractionation $10^3 \times \ln \alpha$ is in general non-linear in $1/T$ or $1/T^2$. These approximations only hold within certain temperature ranges (note that the ranges shown in the figure are somewhat arbitrary and depend on the system considered).

plotted vs. T , $1/T$, and $1/T^2$ (note that the temperature ranges shown in the figure are somewhat arbitrary and depend on the system considered). The bottom line is that for a specific low- and high-temperature range (which depends on the isotopic exchange reaction), $10^3 \times \ln \alpha$ is linear in $1/T$, and $1/T^2$. However, in general it should not be expected that these relationships are the correct ones to fit experimental data. Caution is therefore advised when extrapolating $1/T^n$ -relationships to temperatures beyond those covered by the data.

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